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APPLICATIONS OF SURFACE ANALYSIS
TECHNIQUES TO STUDIES OF ADHESION

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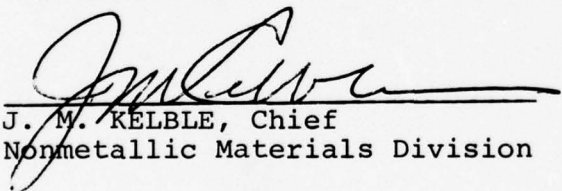
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The question is often asked, "Which is the best surface chemistry tool for research on adhesive bonding?" This question is difficult to answer because it depends on the aspect of adhesion which is being studied. Often a combination of instruments must be used to take advantage of the strong points of each. In metal-to-metal bonding there are many facets of adhesive/adherend interaction. Elemental characterization

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of adherends, especially when composition with depth is desired, is often best accomplished with Auger Electron Spectroscopy (AES). When information of chemical bonding is required, X-Ray Photoelectron Spectroscopy (XPS) is the choice of most workers. Extremely thin layers of material (when first layer surface sensitivity is needed) requires Ion Scattering Spectrometry (ISS). The high sensitivity of Secondary Ion Mass Spectrometry (SIMS) to many elements important in adhesive bonding makes this technique useful, especially coupled with other methods, such as ISS and AES. Modern surface analysis along with Scanning Electron Microscopy (SEM) provides information on failure sur- faces to allow unequivocal determination of the mode of failure. Problems such as charging and decomposition under the probing beam are encountered when characterizing the part of the failure surfaces containing the adhesive.

Although original surfaces and failure surfaces following testing are relatively routinely analyzed, the characterization of the intact bond is not so easy. The interphase region between adherend and adhesive is smaller than the probe, exhibits charg- ing and is unstable. Although no one technique adequately characterizes the bond interphase region, the SEM, the AES micro- probe, and special techniques using Transmission Electron Micros- sopy (TEM), may be used to gain some information about the bond. The more fundamental study of the interaction of polymers and polymer precursors with metals and alloys is carried out by surface energetics measurements, infrared and Raman spectrome- tries, XPS, and electron tunneling spectroscopy.

FOREWORD

This technical report was prepared by W. L. Baun of The
Mechanics and Surface Interactions Branch, Nonmetallic Materials
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Project 2419, "Nonmetallic and Composite Materials," and Work
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Prediction Methodology for Adhesive Bonding." The Work Unit
Monitor was Dr. T. W. Haas.

This report covers work performed inhouse during the period
March 1979 to July 1979 and represents material contained in an
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INTRODUCTION

In an effort to develop strong, light, and corrosion resistant structures, the aerospace industry has gone more and more to adhesive bonding. The automotive industry is quickly following along using different structural alloys. In these fields, bonded structures must be strong and possess long-time durability. Both strength and durability depend on many factors of bond preparation and fundamental properties of the adhesive and adherend. One important influence in the formation of a good adhesive bond is surface or interfacial chemistry. In the broader sense, in which two substances are held together by interfacial forces, adhesion is of importance in many technologies such as in thin films and semiconductors. It is the purpose of this report to discuss methods of surface characterization applicable to the broad area of adhesion with emphasis on adhesive bonding.

SECTION II

DISCUSSION

The question is often asked, "Which is the best surface chemistry tool for research on adhesive bonding?" This question is difficult to answer because it depends on the aspect of adhesion which is being studied. Often a combination of instruments must be used to take advantage of the strong points of each. Table I shows the facets of bonding and some of the characterization methods which are applicable in these areas. Table II is a list of surface techniques from the work of Powell,[1] and the familiar acronyms by which they will be referred to in this work. Many of these methods were described by Park,[2] in a comprehensive review in which he categorized the techniques according to the kind of information they provide. This discussion included what is being probed, such as vibrational states, the probe itself, such as monoenergetic electrons, and what was actually being measured, such as the electron emission.

1. CHARACTERIZATION OF THE ADHEREND

A determination of the chemistry of metallic adherends presents problems of each of the areas discussed here. Many of the surface chemical techniques are applicable to the analysis of adherends, and because of the stability and good conductivity, decomposition, and surface charging are not problems. Surface chemical analysis is usually devoted to (1) determining the amount and distribution of elements purposely placed on the surface to impart a desirable property, and (2) detection and monitoring of impurity elements which may be deleterious to the adhesive bond. Many chemical etching and oxidizing treatments are used on metal and alloys to enhance adhesive bonding of the surface. Enhancement comes about by roughening of the surface and by changing the surface chemistry. In addition, some thermal treatments, such as the bond cure in adhesive bonding, may affect

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TABLE I

ASPECTS OF ADHESIVE BONDING
AND APPLICABLE SURFACE CHARACTERIZATION METHODS

ADHEREND CHEMISTRY

AEAPS, AEM, AES, APS, BIS, CIS, CL, EM, ES,
EXAFS, IIRS, IIXS, IMMA, IS, ISS, LMP, PES,
RBS, SIMS, SXAPS, SXES

ADHEREND STRUCTURE AND MORPHOLOGY

AEM, ELL, EM, HEED, IMMA, LEED, SEM, SIIMS,
SRS, STEM, TEM, XEM, XRD

ADHESIVE CHEMISTRY

AES, AIM, ASW, ATR, ESR, HA, IRS, ISS, LS,
PES, SIMS, UPS, XPS

ADHESIVE STRUCTURE AND MORPHOLOGY

ATR, IR, UV, RAMAN, SEM

INTERACTION OF POLYMERS WITH METALS

AES, AIM, ASW, CPD, ELL, EELS, ESDI, ESDN, FD,
FDS, HA, IRS, IR, ISS, ISD, LEED, LS, PD, SC,
SIMS, UPS, XPS, RAMAN

FAILURE SURFACES (LOCUS OF FAILURE)

AES, ATR, ELL, ISS, SIMS, PES, XPS, SEM,
SXES, SXAPS, SRS, UPS

TABLE II

SURFACE CHARACTERIZATION METHODS
(Ref. 1)

AEAPS	Auger-electron appearance potential spectroscopy	HA	Heat of adsorption
AEM	Auger-electron microscopy	HEED	High-energy electron diffraction
AES	Auger-electron spectroscopy	IIRS	Ion-impact radiation spectroscopy
AIM	Adsorption isotherm measurements	IIXS	Ion-induced X-ray spectroscopy
APS	Appearance-potential spectroscopy	IMMA	Ion microprobe mass analysis
ASW	Acoustic surface-wave measurements	IMXA	Ion microprobe X-ray analysis
ATR	Attenuated total reflectance	INS	Ion-neutralization spectroscopy
BIS	Bremsstrahlung isochromat spectroscopy	IRS	Internal reflectance spectroscopy
CIS	Characteristic isochromat spectroscopy	IS	Ionization spectroscopy
CL	Cathodoluminescence	ISD	Ion-stimulated desorption
COL	Colorimetry: IR, visible, UV, X-ray, and γ-ray absorption spectroscopy	ISS	Ion-scattering spectroscopy
		ITS	Inelastic tunneling spectroscopy
CPD	Contact potential difference (work-function measurements)	LEED	Low-energy electron diffraction
DAPS	Disappearance-potential spectroscopy	LMP	Laser microprobe
EL	Electroluminescence	LS	Light scattering
ELL	Ellipsometry	MBRS	Molecular-beam reactive scattering
EELS	Electron energy-loss spectroscopy	MBSS	Molecular-beam surface scattering
EM	Electron microprobe	MOSS	Mössbauer spectroscopy
ES	Emission spectroscopy	NIRS	Neutral impact radiation spectroscopy
ESDI	Electron-stimulated desorption of ions		
ESDN	Electron-stimulated desorption of neutrals	NMR	Nuclear magnetic resonance
		NRS	Nuclear reaction spectroscopy
ESR	Electron-spin resonance		
EXAFS	Extended X-ray absorption fine structure	PD	Photodesorption
		PEM	Photoelectron microscopy
FD	Flash desorption	PES	Photoelectron spectroscopy
FDM	Field-desorption microscopy	RBS	Rutherford backscattering spectroscopy
FDS	Field-desorption spectroscopy		
FEM	Field-emission microscopy	RHEED	Reflection high-energy electron diffraction
FEES	Field-electron energy spectroscopy		
		SC	Surface capacitance
FIM	Field-ion microscopy	SDMM	Scanning desorption molecule microscopy
FIM-APS	Field-ion microscope - atom probe spectroscopy		
		SEE	Secondary-electron emission
FIS	Field-ion spectroscopy	SEM	Scanning electron microscopy
GDMS	Glow-discharge mass spectroscopy	SEXAFS	Surface extended X-ray absorption fine structure

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TABLE II (Continued)

SURFACE CHARACTERIZATION METHODS
(Ref. 1)

SI	Surface ionization
SIIMS	Secondary-ion imaging mass spectroscopy
SIMS	Secondary-ion mass spectroscopy
SLEEP	Scanning low-energy electron probe
SRS	Surface reflectance spectroscopy
STEM	Scanning transmission electron microscopy
SXAPS	Soft S-ray appearance - potential spectroscopy
SXES	Soft X-ray emission spectroscopy
TE	Thermionic emission
TEM	Transmission electron microscopy
TL	Thermoluminescence
UPS	Ultraviolet photoemission spectroscopy
XEM	Exoelectron microscopy
XES	Exoelectron spectroscopy
XPS	X-ray photoemission spectroscopy
XRD	X-ray diffraction (glancing incidence)

the composition of the surface, either by introducing impurities or by increasing or decreasing a concentration of alloying elements at the surface. McDevitt and co-workers used a number of complementary modern surface analysis tools to analyze several aluminum alloys following chemical treatment for adhesive bonding.[3,4,5] They found a number of interesting phenomena, including the one illustrated in Figure 1, where the formation of an interfacial region rich in copper is shown on 2024 aluminum alloy. The concentration and width of this potential weakened boundary layer is found to vary depending on the etching conditions of the chromic acid-sodium dichromate solution. This solution is related to the surface preparation method known as the FPL etch. Similar results were obtained more recently by Sun and co-workers.[6] The formation of such potential weak boundary layers may influence both the initial bondability and the long time durability of the adhesive bond. Baun, et al.[7] used ISS, SIMS, and AES to analyze a variety of metal and alloy adherends. These authors also used several surface treatments on titanium and titanium alloys and analyzed them by surface techniques such as ISS, SIMS, AES, and SEM.[8,9,10] Large differences in chemistry were observed on titanium and its alloys depending on the surface treatments. An example similar to the phosphate fluoride treatment on titanium commercial purity is shown in Figure 2. This ISS and positive SIMS data indicate that substantial amount of fluorine is present on the surface. The cluster or fingerprint spectra in the SIMS data suggests that titanium fluoride is actually present on the surface. The cleanliness and wetability of adherend surfaces may be inferred by classical methods such as contact angle measurements,[11] ellipsometry,[12] and contact potential difference measurements.[13] A combination of these techniques was used by Smith in a program related to the analysis of adhesive bonding materials.[14]
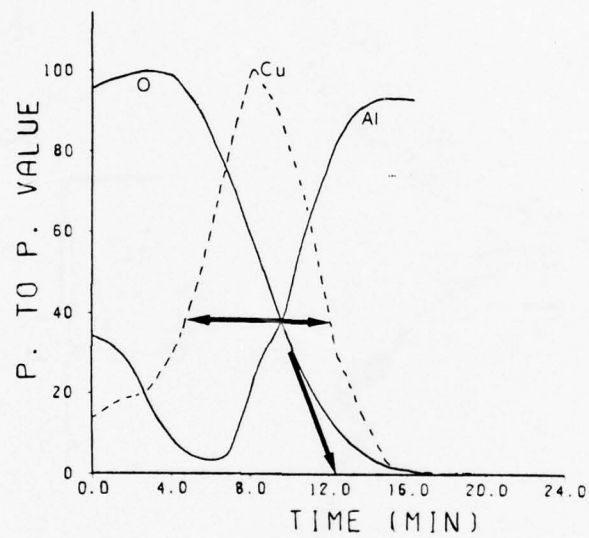
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Figure 1. Normalized elemental profiles for aluminum, oxygen, and copper from 2024 aluminum alloy treated with FPL etch.
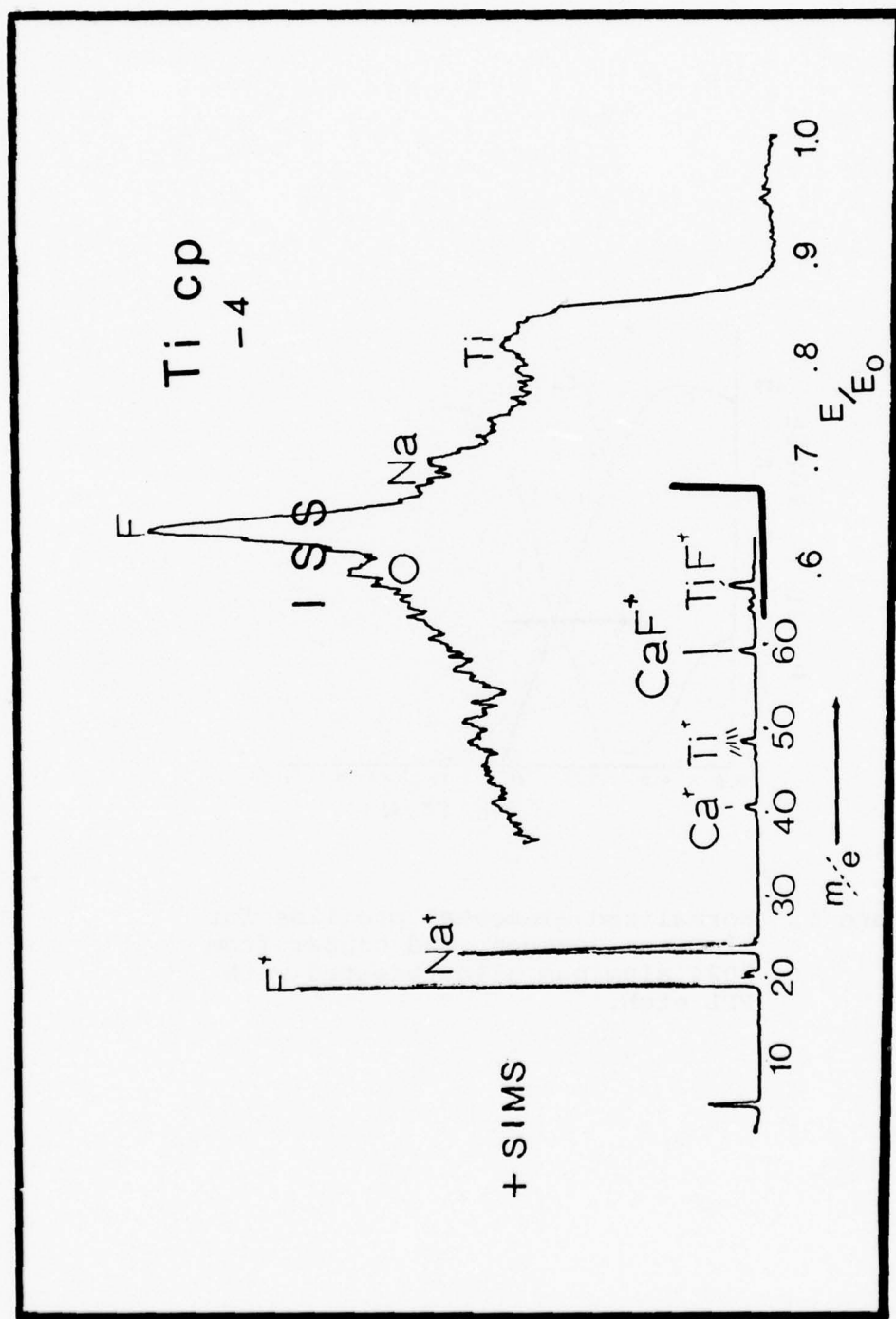
Figure 2. ISS-SIMS data for titanium treatment as follows: Sample submerged in a solution of 50 grams sodium orthophosphate, 9 grams sodium fluoride, 26 milliliters of hydrofluoric acid and distilled water to make 1 liter. Rinse in running tap water and deionized water.

Generally, the metallic adherend is covered by a layer of
oxide on the surface. Since this layer of oxide is the surface
to which the adhesive comes in contact, the structure and thick-
ness of this oxide is extremely important. Several methods are
available for determining the thickness of oxides on metals. An
extremely accurate method when surfaces are very flat and smooth,
is the ellipsometer. Optical interference methods are very
simple and provide accurate answers for many materials. More
recently, scanning electron microscopy has been applied to the
measurement of thicknesses by bending the specimen until the
oxide film breaks and then observing the broken film. Such work
is illustrated by the research done by Remmel which provided not
only the thickness of oxides on aluminum alloys but also an
acceptance classification for the oxide.[15] A very useful method
which both chemical data and thickness information is gained is
the sputter-etching method. This technique uses a beam of noble
or active ions to slowly etch away the surface. The same beam
or another sampling beam provides chemical information with
depth. Rastering and gating techniques of the ion beam mini-
mize crater edge effects. An AES elemental profile for titanium
and oxygen from commercial purity titanium is seen in Figure 3.
The sputtering time as shown in this figure can be equated to
oxide thickness by the use of standard oxide samples prepared by
anodization methods.

Some elemental analysis techniques allow the determination
of electronic structure of the solid surface by probing core
level electrons.[16] These methods include characteristic iso-
chromat spectroscopy, soft x-ray appearance potential spectros-
copy, and x-ray photoelectron spectroscopy. By far, the most
popular of these techniques has been XPS. The XPS technology
allows core level binding energies to be routinely measured and
line shapes studied to allow the determination of chemical bonding
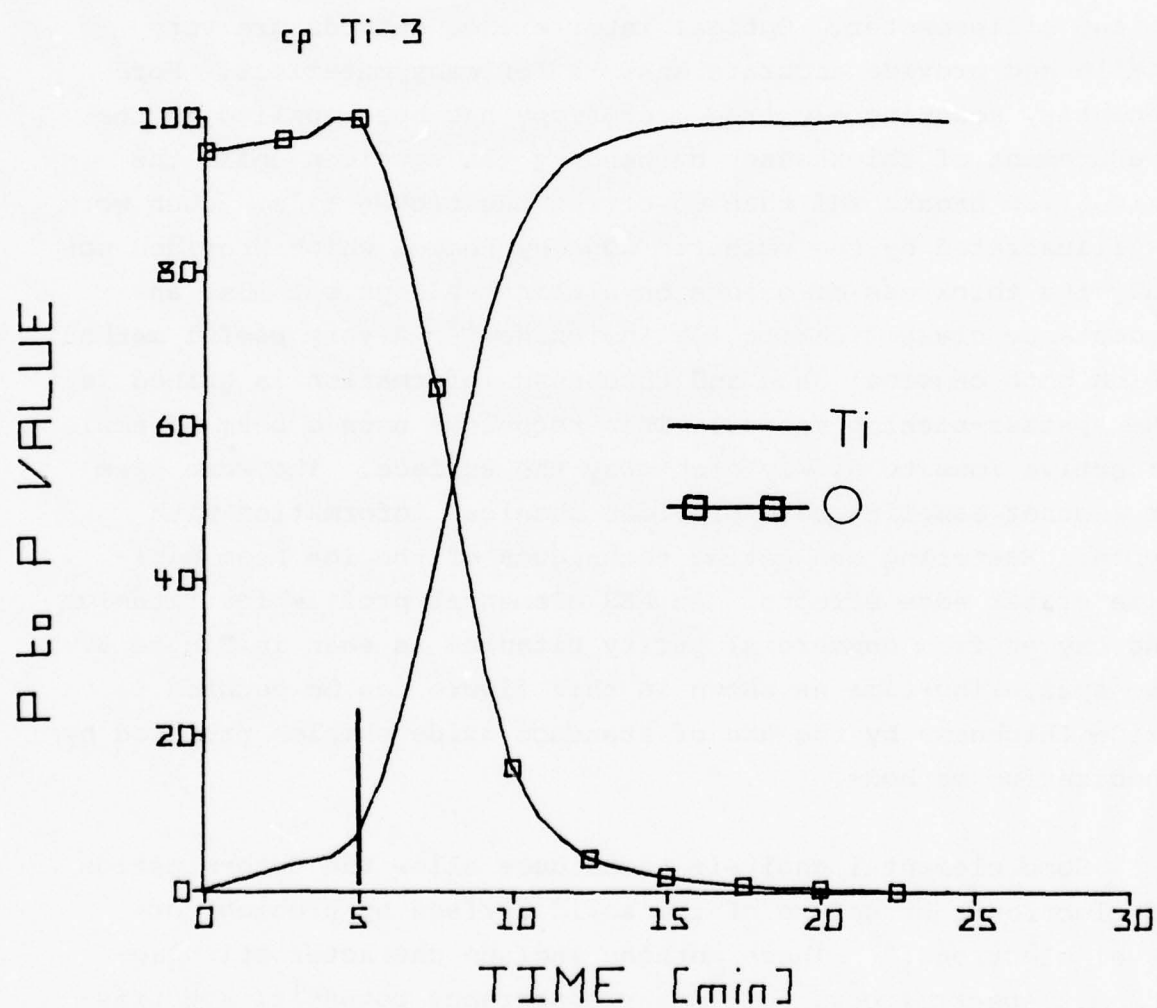
Figure 3.   AES elemental profile for Ti and O from TiC.P.
given nitric/hydrofluoric acid etch.

at the surface. Practical use of this technique is shown in
Table III from work of Van Ooij.[17] Here the XPS results were
used for the development of an adhesion model of rubber to
brass. They were combined with quantitative data on adhesion
of samples with different properties or compositions. Some
experiments were conducted to evaluate the adhesive properties
of materials other than brass. A summary of these results is
given in this table. The conclusion that was reached was that
high adhesion level can only be obtained with brass of 60-70%
copper, with pure copper layer of thickness less than 50 nm or
with a thin copper sulfide layer.

In many adhesive bonding systems, the morphology of the
oxide on the adherend is all important. Such is the case with
the phosphoric acid anodize for aluminum used for commercial
adhesive bonding in the aerospace industry. It has been found
that the formation of a porous structure is necessary for good
bondability and durability. Determination of oxide morphology
is best accomplished by scanning electron microscopy. An example
of the columnar or porous structure seen in phosphoric acid
anodized on 2024 aluminum alloy is shown in Figure 4.[18]

Although oxide growth morphology is relatively easy to
determine using the scanning electron microscope, the determina-
tion of actual structure is not that simple. Most oxides formed
at low temperature and particularly oxides formed in anodizing
solutions tend to be very poorly crystalline (nearly "amorphous").
They may be very highly impurity stabilized and contain many
defects. Therefore, conventional methods of analysis which
depend on highly crystalline lattices, such as electron diffrac-
tion, do not provide much information on thin oxide films used
in adhesive bonding. Likewise, x-ray diffraction provides little
information on thin films because of the high penetration. Special

TABLE III

ADHESION OF SOME SELECTED MATERIALS TO RUBBER[a]

Material	Adhesion level[b]	XPS of interface	Remarks
1. iron, steel	0	-	no adhesion
2. copper sheet	0	excess Cu_2S	some adhesion if undercured
3. copper-plated steel[c]	700-900	-	good adhesion if plating thickness <50 nm
4. steel + Cu_2S coating[d]	700-800	-	good adhesion for fresh Cu_2S layer (<50 nm)
5. zinc sheet	100-200	ZnS formation	poor adhesion
6. copper-plated zinc[c]	700-800	Cu_2S formation	good adhesion if plating thickness <50 nm
7. 70/30 brass sheet	700-1000	formation of Cu_2S and ZnS	good adhesion; level depends on surface preparation

a Vulcanized at 150°C for 25 min.
b In N/64 mm².
c By electroless immersion plating.
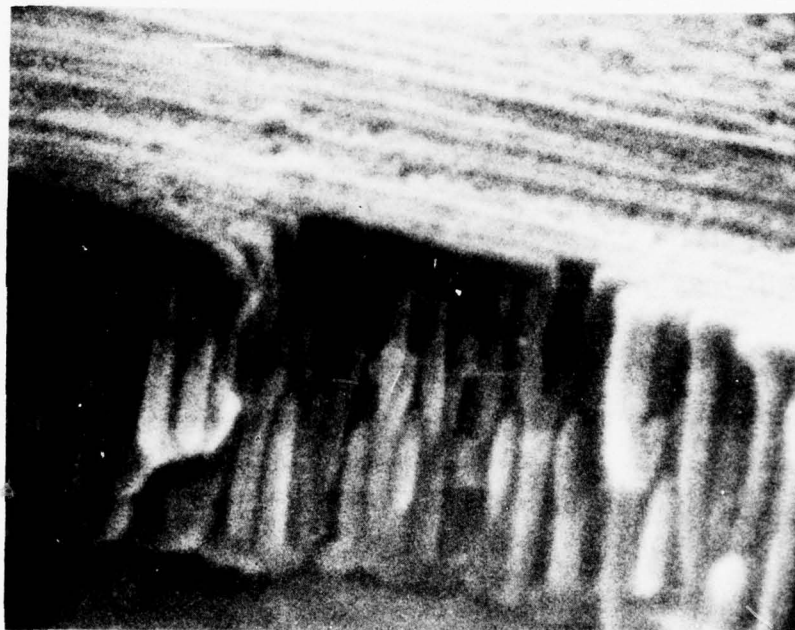d Prepared from sample 3 by reaction with sulfur in liquid paraffin at 180°C.

Figure 4. Scanning electron micrograph showing oxide columnar structure of phosphoric acid anodized aluminum.

techniques utilizing grazing incidence and focusing methods, such as the Seeman-Bohlin method may be used to improve surface sensitivity, but the lack of crystallinity of most films still poses problems. Such conventional techniques as x-ray diffraction should not be abandoned, however, since some effects such as stress due to mechanical working of the surface may show up in fine features of the diffraction pattern, such as peak broadening or intensity variations.

2. CHARACTERIZATION OF THE ADHESIVE

Characterization of the chemistry and morphology of the adhesive is somewhat more difficult than for the adherend. Since the adhesive is generally nonconducting when it is bombarded with charged particles or electrons, the surface charges and causes problems in surface chemical analysis. Methods of charge neutralization are available which minimize this problem. For instance, in ISS and SIMS a flood of low energy electrons removes the positive charge caused by the bombardment of ions on the surface. In techniques such as XPS, charging is not so severe but still remains a problem. XPS appears to be the technique most used for characterization of the adhesive because of the large amount of data which it provides. Table IV shows the principal features in the XPS spectra of polymers, and the information that can be gained from these features.[19] Numerous XPS results have established that absolute and relative binding energies and relative peak intensities are capable of elucidating many important aspects of polymer surface chemistry. New work on low intensity shake-up satellite peaks, located a few electron volts higher in binding energy than the main peak, have been assigned to $\pi \rightarrow \pi^*$ transitions. This is a new characteristic feature in the spectra of unsaturated polymers and offers a potential for new insight into π electron distribution. Dwight and co-workers have performed detailed analyses of photoelectron spectra of hydrocarbons and other complex molecules,[19] and of fluorocarbons.[21,22]

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TABLE IV

PRINCIPAL FEATURES IN THE XPS SPECTRA OF POLYMERS
(Ref. 19)

Spectral Feature	Information
I. Main Peak Position	Atom identification
II. Chemical shift	Oxidation state
III. Peak area ratios	Stoichiometry
IV. Shake-up satellites	$\pi \rightarrow \pi^*$ Transitions

Many polymers show PES features that are a combination of two or more valence states such as the example shown in Figure 5, the carbon 1s levels from Mylar.[19] The main peak at 285 eV is assigned to the six carbons from the benzene ring, the peak at 286.8 eV to the two ester carbons, and the third peak at 289 eV to the two carboxyl groups. At 291.5 eV, a low intensity shake-up satellite arising from the aromatic ring can be resolved. By detailed analysis and deconvolution of such spectra, very small changes in polymer structure may be deduced.

The molecular spectroscopy techniques, infrared spectroscopy and Raman spectroscopy, are used to determine small changes in polymer surfaces by reflection techniques. Two major recent developments have improved the state of the art of molecular spectroscopy. One development was that of the Fourier transform in infrared spectroscopy, mostly due to the availability of computer techniques and the wide-spread use of interferometer methods in infrared. In Fourier transform infrared, all infrared signals are observed simultaneously and the resultant signal or interference pattern is transformed into a standard spectral distribution by Fourier analysis. The other development is that of the laser as a Raman source. The additional energy available in the laser source has enabled recording of the spectra from many solid surfaces. An example of the use of Raman spectroscopy is seen in Figure 6 where the 1096 cm^{-1} line is shown from Mylar. The effect of crystallinity is seen here by a narrowing of the band in the crystalline polymers.[23] Similar effects are observed in reflection infrared spectra. Reflection-absorption infrared spectra coupled with ellipsometry has been used to study epoxy films on metals.[24] The spectra from this work suggests that the thin films deposited on the metal from solution probably were adsorbed with a vertical confirmation with only a single bond to the surface. The latter work is an
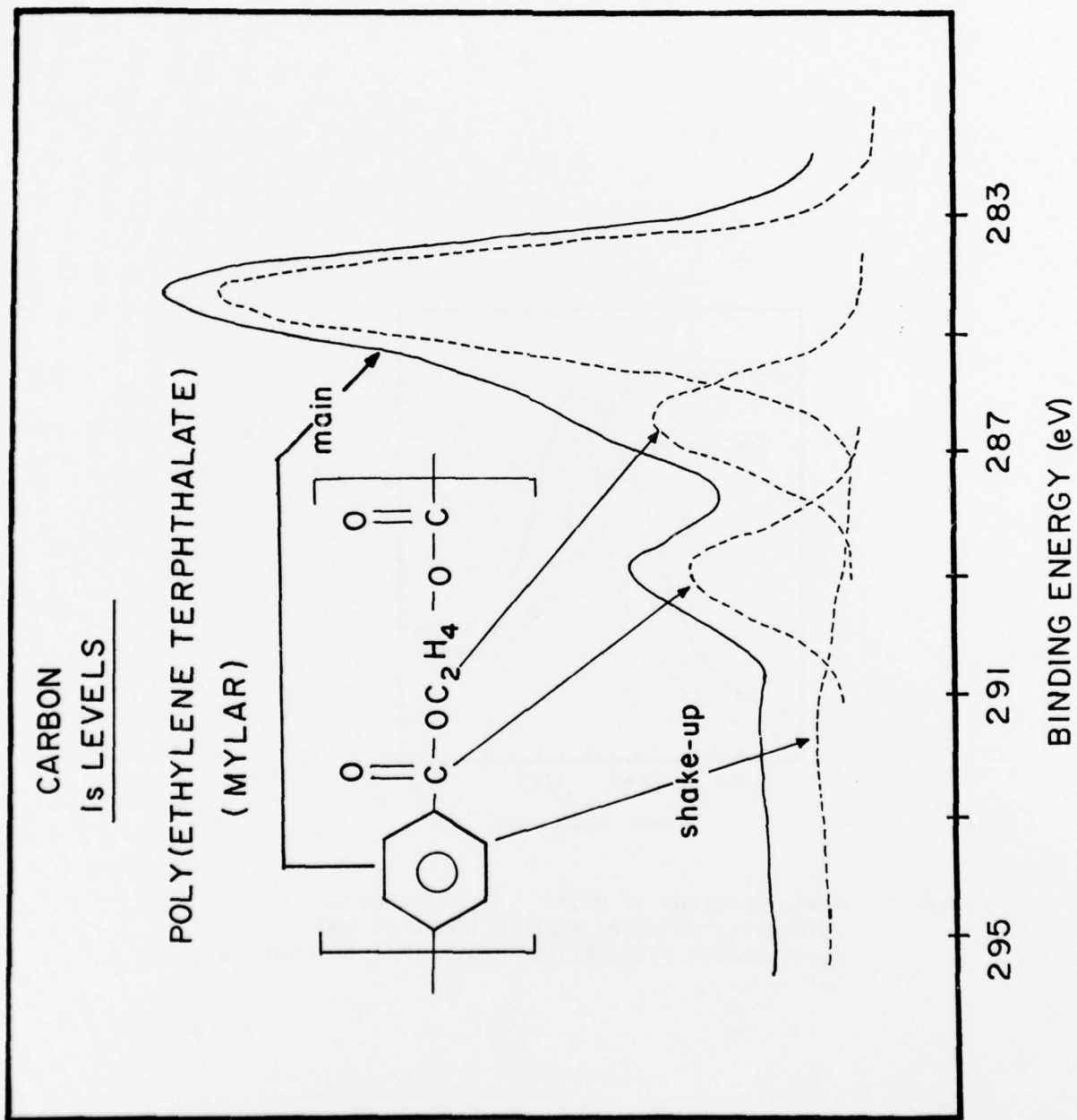
Figure 5. Carbon 1s XPS spectrum from polyethylene terephthalate (Mylar) film.
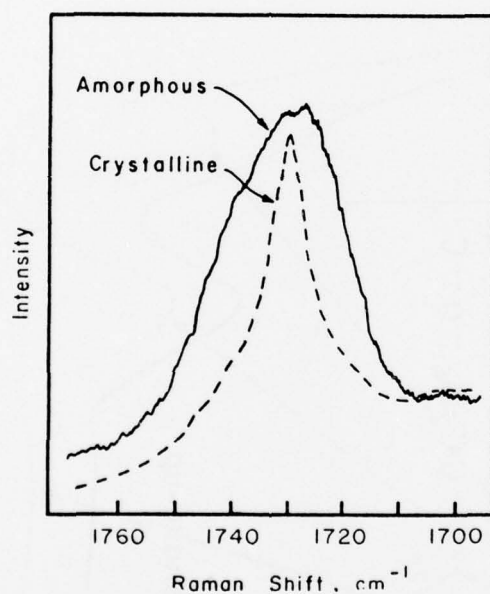
Figure 6.   Raman Spectrum of Mylar - (Appearance of the
carbonyl stretching band of quenched and
crystallized polyethylene terephthalate from
Ref. 23).

example of the study of the structure of the adhesive and its
alteration upon interaction with the adherend. This interaction
of the polymer with the metal or alloy is studied or indirectly
inferred by adsorption, desorption, contact angle, XPS, electron
tunneling, x-ray excited AES, and radioactive tracer methods.
It appears that XPS provides the most powerful method for deter-
mining bonding of organic materials on oxidized surfaces. An
example of such work is the research of Anderson and Swalen,[25]
who studied the bonding of various organic monolayers on oxidized
surfaces. They found that with successive applications of
different amounts of soap films applied by the Langmuir-Blodgett
technique to oxidized metal surfaces that progressive changes
were observed in the x-ray photoelectron spectra from the ele-
ments in the oxides. They also found that the binding energies
and peak shape changed in the soap film overlayers, suggesting
partial transfer of charge, such as an acid-base interaction.[25]

Although there are numerous methods to study the inter-
action of the adhesive with the adherend, there are very few
methods which allow the direct study of the intact bond. Even
the SEM methods are not simple because the adhesive area is
an insulator and tends to charge. In order to obtain good SEM
pictures frequently the adhesive bond must be coated with a
thin film of a conductor, such as gold or gold-palladium alloy.
Nondispersive x-ray emission analysis may be performed either
in a microprobe or in the SEM, but generally the elements which
may be determined are limited to elements heavier than fluorine.
Elements such as carbon and oxygen which are of considerable
interest in adhesive bonding studies give x-ray emission spectra
which are of too long a wavelength to be detected by conventional
detectors. The AES microprobe which usually allows spacial analy-
sis of surface elements of approximately 5 μm, also is plagued by
the problem of surface charging on intact bonds. Special TEM

methods using ultra microtomy may provide some structural information but do not provide any chemical data. Conventional replication methods on intact bonds may be used to study the interaction of adhesive and adherend as illustrated in Figure 7. Here it appears that the adhesive has not penetrated the pores of the phosphoric acid anodized oxide on 2024 aluminum alloy.

3. FAILURE SURFACES

The strength of an adhesive joint measured by means of numerous physical tests which place the joint in shear or tension or a combination of the two. These tests, in which an increasing load is placed on the joint until failure occurs, give some idea of the initial bondability of an adhesive-adherend combination. Similar tests in which the bond is under load but at high temperatures and humidity are accelerated tests of bond durability. In the past, following joint failure, visual or sometimes microscopic examination of the failure surfaces was made to determine the mode of failure. A major consideration in identifying the mechanics of adhesive joint failure is the locus of fracture, whether the joint failed by (1) cohesive fracture of the adhesive, (2) adhesive failure interfacially between the adhesive substrate interface, or (3) a complex mixture of possible failure modes. A long-time theory held by Bikerman[26] says that true interfacial failure occurs so seldom that this failure mode need not be treated in any theory of adhesive joints. He says that apparent failures in adhesion are quite common but they take place in a weak boundary layer so near the interface that the adhesive remaining on the adherend after the rupture is not visible. Such failures at a weak boundary layer have been analyzed by ISS-SIMS.[27,28,29] In that work it was shown that when the SEM and spectro-chemical tools are used to determine the morphology and the chemical species on the surface there still may be difficulties in interpreting the location of failure.
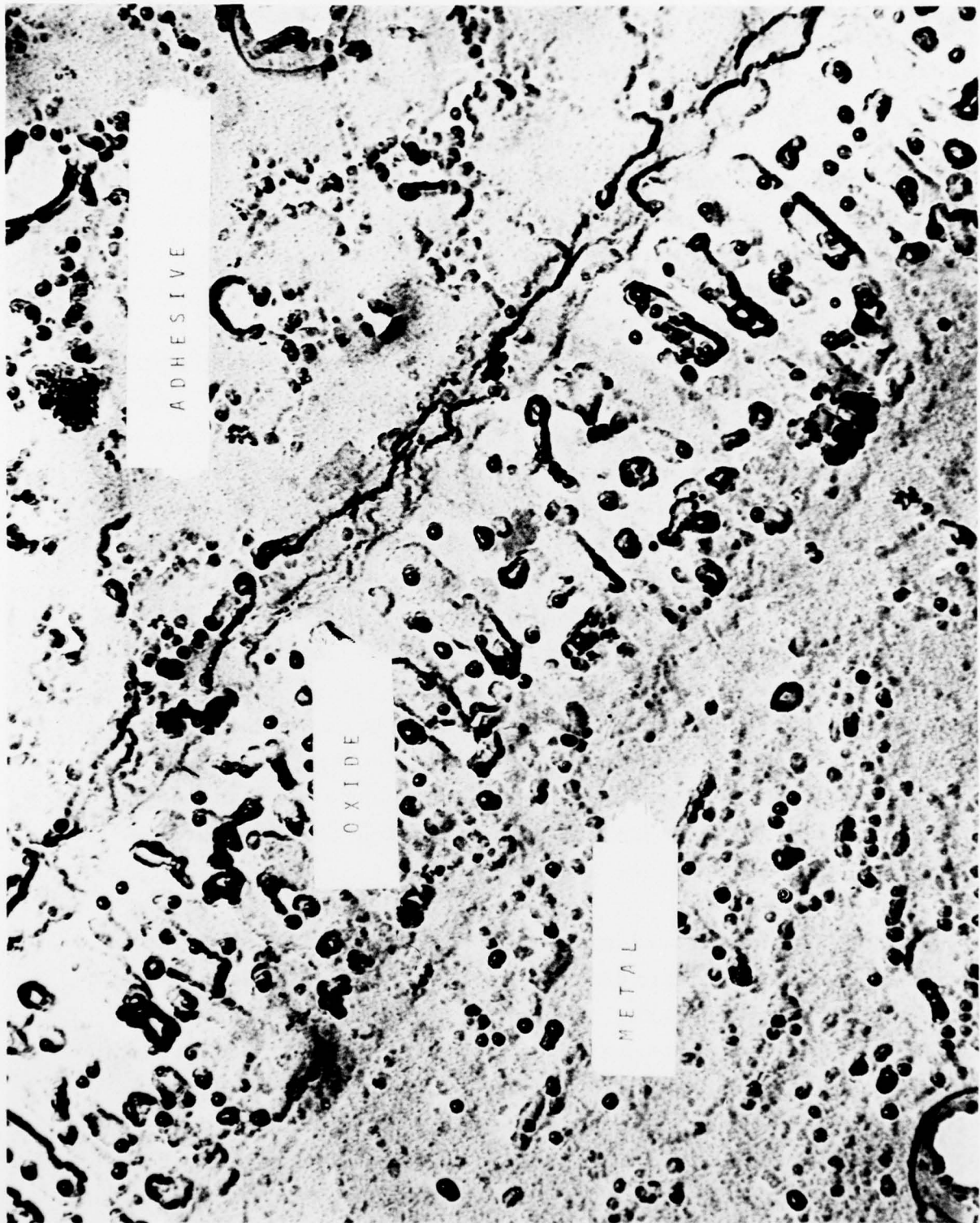
Figure 7. Transmission electron micrograph of a replicated surface of phosphoric anodized aluminum surface.

Some failures are very clear cut while in others, particularly
mixed mode failures, the interpretation may not be as easy.
Figure 8[28] shows a typical complex adhesive bonded system in
which several interfacial regions exist. Each of the materials
coming together to form these interfaces has its own individual
chemical signature. The substrate, for instance, usually con-
tains alloy elements which vary in content between the surface
and the bulk. In addition to alloying elements, surface treat-
ments leave behind elements characteristic of each treatment.
For instance, the popular etch used for aluminum alloys, con-
sisting of sulfuric acid and sodium dichromate in distilled water,
leaves a detectable amount of chromium on the alloy surface.
Primers often contain anion and cation which can be followed by
spectro-chemical methods. Such additives, such as strontium
chromate are usually placed in the primer to provide corrosion
protection in the coating. The adhesive often contains fillers
such as aluminum or aluminum oxide to provide conductivity or
to match coefficient of thermal expansion. Using these differ-
ences in chemistry, it was possible[28] to determine a failure
mechanisms occurring in a thick-thin wedge specimen designed to
concentrate stresses along the interface. This work showed an
initial locus of failure which changed during the period of
testing at high temperature and humidity.

In addition to determining what elements exist on failure
surfaces, it is most important to look at these surfaces using
optical microscopy and SEM. Dwight and co-workers[30] have used
the SEM extensively, especially in cohesive failures to attempt
to understand the mechanism by which failure occurs. Plastic
and brittle failure mechanisms are easily differentiated in
the polymer surface. Initial and final flaws and voids may be
determined and are of importance in evaluating joint performance.
Some of these features which may be observed by microscopic
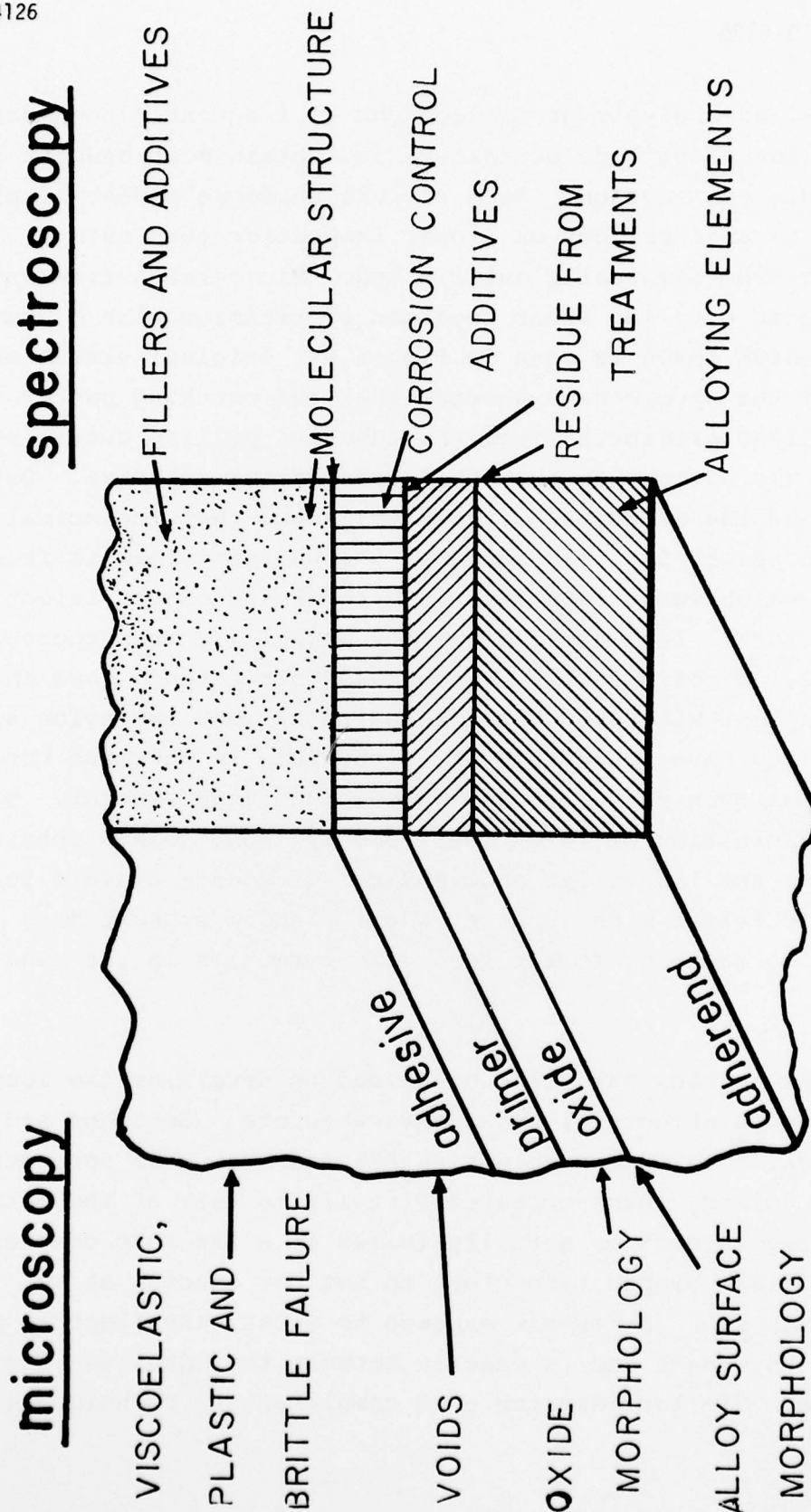techniques are shown in Figure 8.

Figure 8. A typical complex adhesive bond and the role of microscopy and spectroscopy in the study of the materials and interfaces of that bond.

Detailed analysis of micrographs is frequently necessary
to determine exact mode of failure and obtain most benefit from
microscopic examination. Some failure surfaces appear simple
and easy to analyze, but on closer inspection turn out to be
different from originally anticipated. Micrographs from match-
ing surfaces of a lap shear specimen of titanium with a commer-
cial adhesive FM400 is seen in Figure 9. Original visual exami-
nation of the specimens suggested that the matching patterns
on both sides originated from the adhesive pulling out in the
areas of the pattern on the other side of the adhesive. Detailed
analysis of the micrographs, however, shows that the actual joint
contained nearly 50% void and that the pattern shown is from the
adhesive which was originally along the knots of the tricot
carrier cloth. Such air entrapment, especially on supported
adhesives, is not unusual. Bascom and Cottington[31] have shown
air entrapment with structural adhesive films using nylon support
cloth. They have found that it is possible to increase bond
strength as much as 30 percent by complete void removal. Micro-
scopic examination of 14 typical adhesive bond joints obtained
from aerospace industries showed varying amounts of void forma-
tion in adhesives with support cloth. Random support mats
appeared to cause or foster less void formation in the bond
line.

Other methods have also been used to determine the locus
of failure in structural and adhesive joints. Gettings and
co-workers,[32] using a combination AES and XPS, have demonstrated
that the joints, which appeared visually to fail at the metal
oxide-epoxy interface, actually failed in a far more complex way
with the crack propagating close to but not exactly at the inter-
face. When such joints are exposed to water, the fracture path
is found to change and is exactly between the adhesive-metal
interface. Similar research used complementary techniques, XPS
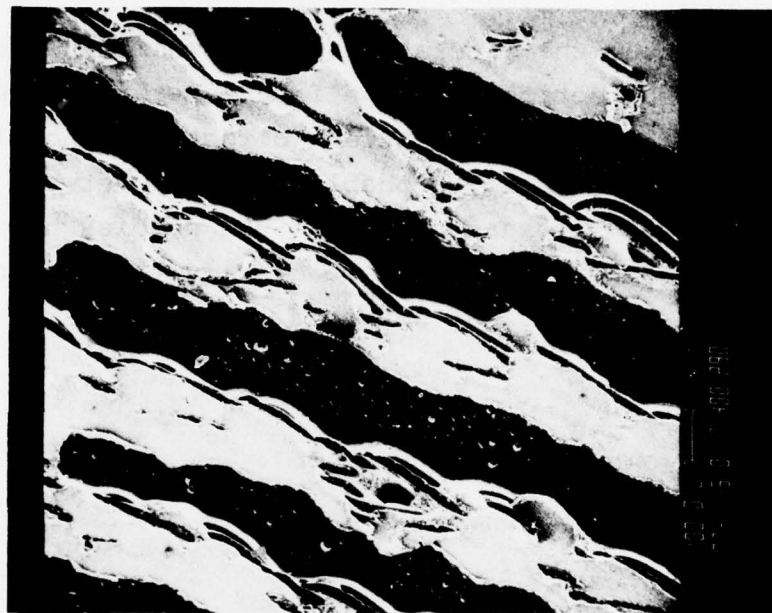
24

FM 400

LAP SHEAR

Figure 9. Scanning electron micrographs of matching failure surfaces from a lap shear specimen of Ti6Al4V - FM400 adhesive.

and SIMS, to study the interaction of polysiloxane-metal oxide interfaces.[33] Detection from the iron adherend of $FeSiO^+$ radicals from the primer has strong direct evidence for the formation of a chemical bond, probably Fe-O-Si, between the metal oxide and the polysiloxane primer. Such studies not only elucidate the locus of failure but also clarify the fundamental processes between adhesive and adherend.

SECTION III
CONCLUSIONS

Spectro-chemical techniques combined with microscopy can usually be used to **analyze the adherend and adhesive surfaces** and to gain a clear picture of where an adhesive joint failed during testing or service. Methods are also available for studying the fundamental interaction of polymers and polymer precursors with metals and metal oxide surfaces. The study of the undisturbed adhesive bond, however, is more difficult. Few techniques really tell very much about the intact bond, and a definite need exists for such methods.

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